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Organometallic Compounds

XIII*. Topological Representations of Intramolecular Rearrangements of Six-Coordinate Structures

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Topological representations for the intramolecular isomerizations of octahedral complexes are given. The number of dimensions which have to be used for this description depends on the complexity of the chemical system and becomes too great for some of the most general cases to be useful in practice. Therefore, another model is given, where the chemical transformations are represented by permutations of structures located at the edges of triangular faces of a hypertetrahedron.

Für die intramolekulare Isomerisierung oktaedrischer Komplexe werden topologische Darstellungen angegeben. Die zur Beschreibung notwendige Dimension wird für kompliziertere chemische Systeme zu groß, um von praktischem Nutzen zu sein. Deshalb wird ein anderes Modell beschrieben, bei dem die chemischen Umwandlungen durch Permutationen von Strukturen dargestellt werden, die an den Ecken von Dreiecksseiten eines Hypertetraeders lokalisiert sind.

Représentations topologiques pour les isomérisations intramoléculaires des complexes octahédriques. Le nombre de dimensions nécessaires à cette description dépend de la complexité du système chimique et devient trop grande pour certains des cas les plus généraux pour être utile en pratique. Cependant, on donne un autre modèle où les transformations chimiques sont représentées par des permutations de structures placées aux arêtes des faces triangulaires d'un hypertétraèdre.

Muetterties [2] has described a topological representation for the interconversions of a given octahedral complex ML_6[1], into its 29 other possible isomers. The trigonal twist used as reaction pathway goes through trigonal prismatic intermediates or transition states [3]. This author suggests the use of a dodecahedron with edge midpoints and lines connecting adjacent and non adjacent edge midpoints in each pentagonal face respectively to represent the 30 complexes and the 120 trigonal prismatic intermediates or transition states.

We wish to introduce a series of representations for some simpler systems, to show how these representations evolve when the complexity of the system is progressively increased, and to extrapolate these results to the general case.

Numbering Convention and Description of the Trigonal Twists

The numbering convention will be that outlined by Muetterties [4]: first one gives the three ligands which define the triangular face which has the lowest number, going clockwise when the face is directed towards the observer; then one writes

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* For part XII, see Ref. [1].

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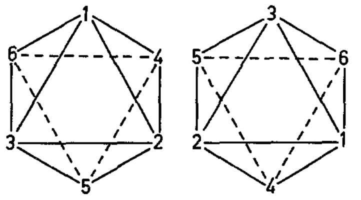
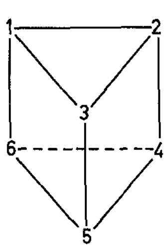
[1] ML_6, denotes a metal M surrounded by six ligands which can be distinguished.

the other three substituents, beginning with the ligand which is located at the right of the first one, and turning clockwise again.



The enantiomer of a given isomer is obtained by a permutation of the third and fourth digits: the optical antipode of 123,456 (*O*) is thus 124,356 ($\bar{O}$).

It is also important to describe the possible intermediate complexes or transition states. For these trigonal prisms [4], the convention is the same as that for the trigonal antiprisms (or octahedra undergoing a trigonal twist), starting the numbering of the second face with the ligand which is located above the ligand cited first on the first face. The letter *P* is written before the symbol of prismatic structure to distinguish between prisms and octahedra will be denoted *P* 123,645 and its enantiomorph is obtained by the permutation of the last two figures[2] of each triangular face, thus *P* 132,654.



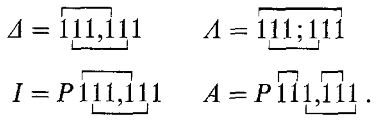
Rotations of triangular faces in the octahedron, called RC_3 by Muetterties [2], transform, one isomer into *eight* other ones. The isomers obtained from $(O) = 123{,}456$ by the eight possible trigonal "Bailar-type" (3) twists[3] are thus

$$(1) = 123{,}645;\quad (2) = 123{,}564;\quad (3) = 125{,}463;\quad (4) = 126{,}435,$$
$$(5) = 136{,}425;\quad (6) = 125{,}643;\quad (7) = 126{,}534 \text{ and } (8) = 135{,}426.$$

Description of Some Tris-Chelate Systems

The simplest complex possessing three bidentate ligands, 111,111, is described as follows

Fig. 1



$$\Delta = 111{,}111 \qquad \Lambda = 111;111$$
$$I = P\,111{,}111 \qquad A = P\,111{,}111\,.$$

For 112,222, one has

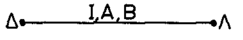
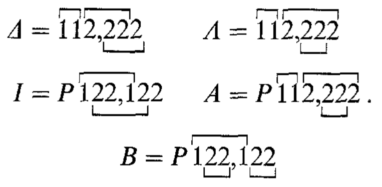


Fig. 2



$$\Delta = 112{,}222 \qquad \Lambda = 112{,}222$$
$$I = P\,122{,}122 \qquad A = P\,112{,}222\,.$$
$$B = P\,122{,}122$$

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[2] When the first two figures of the first face are identical, one uses a permutation of these two figures and of the first two of the second face. In some special cases, one has to permute the two faces (P124, 123 → P123, 124 or P123, 132 → P132, 123). Sometimes, it is necessary to re-number the system after this operation (P124, 231 → P231, 124 ≡ P123, 412 or P123, 241 → P241, 123 ≡ P124, 312).

[3] The description given here for the isomerization is also valid for systems racemizing through the Ray and Dutt rhombic twist [3], which gives the same octahedral reaction products and prismatic intermediates as the Bailar twist used in this paper.

The system 123,333 may also be described by an analogous one-dimensional representation

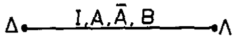

Fig. 3

$\Delta = 123,333 \qquad \Lambda = 123,333$

$I = P\,133,233 \qquad B = P\,133,233$

$A = P\,132,333 \qquad \bar{A} = P\,123,333\,.$

The case 112, 323 will be examined later on.

The 111,222 tris-(1-2)-chelate system has four isomers [5] and a two-dimensional representation is needed. The tetrahedron suggested by Muetterties [2] is however not necessary; a square is sufficient, and is even more suited, as will be seen later.

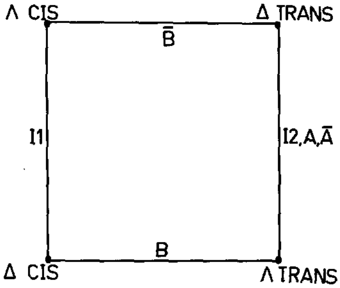

Fig. 4

$\Delta_{\text{cis}} = 111,222 \qquad \Lambda_{\text{cis}} = 111,222$

$\Delta_{\text{trans}} = 112,221 \qquad \Lambda_{\text{trans}} = 112,212$

$I_1 = P\,111,222 \qquad A = P\,112,221$

$I_2 = P\,112,221 \qquad \bar{A} = P\,112,221$

$B = P\,112,122 \qquad \bar{B} = P\,112,212\,.$

The 123,434 case will be described later, but may also be represented by such a square bi-dimensional representation.

The 123,545 case is more complicated: eight isomers are found and a three-dimensional cubic representation (or its two-dimensional projection: see Fig. 5) must be used.

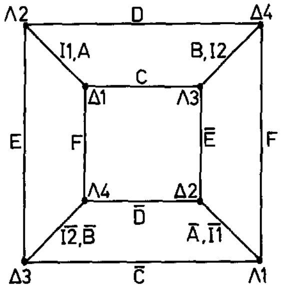

Fig. 5

$\Delta_1 = 123,545$

$\Lambda_1 = 125,345$

$\Delta_2 = 125,453$

$\Lambda_2 = 124,553$

$\Delta_3 = 124,535$

$\Lambda_3 = 125,435$

$\Delta_4 = 125,354$

$\Lambda_4 = 123,554$

$I_1 = P\,135,245$

$I_2 = P\,154,253$

$A = P\,152,354$

$B = P\,125,435$

$C = P\,155,234$

$D = P\,143,255$

$E = P\,124,553$

$F = P\,132,545$

The most general tris-chelate system 123,645 is formed by sixteen isomers and has been described by Muetterties [2] by a four-dimension hypercube.

Thus one sees that, the more complicated the system, the more dimensions are needed for a topological description of the possible isomers and interconversions.

Description of Certain Other Systems

Another way to increase the number of structures and rearrangement pathways is to decrease the number of interligand bonds in a given system.

The tris-chelate 112,324 exists under four different forms and the following topological description of the possible intramolecular rearrangements may be given (see Fig. 6).

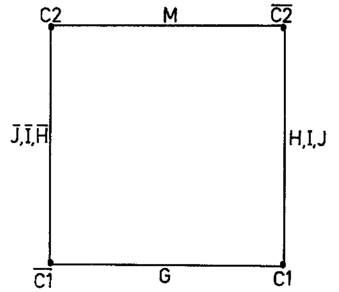

Fig. 6

$C_2(=\Lambda_2) = 112{,}342$ $\bar{C}_2 = 112{,}324$

$C_1(=\Lambda_1) = 112{,}432$ $\bar{C}_1 = 112{,}423$

$H = P\,112{,}432$ $\bar{H} = P\,112{,}342$

$I = P\,124{,}123$ $\bar{I} = P\,123{,}124$

$J = P\,122{,}134$ $\bar{J} = P\,122{,}143$

$M = P\,113{,}224$ $G = P\,114{,}223$

Two other bis-chelate systems (112,324) give racemization paths which may be described by a square pyramid or its two-dimensional projection

112,324 112,324

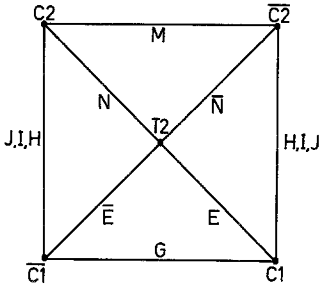

Fig. 7a

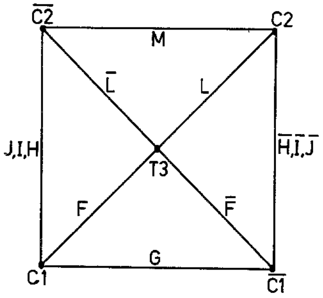

Fig. 7b

$T_3 = 113{,}422$ (see also Fig. 6) $T_2 = 112{,}234$

$L = P\,113{,}422,$ $\bar{L} = P\,113{,}242,$ $N = P\,112{,}234,$ $\bar{N} = P\,112{,}324,$

$F = P\,114{,}322,$ $\bar{F} = P\,114{,}232,$ $E = P\,112{,}243,$ $\bar{E} = P\,112{,}423.$

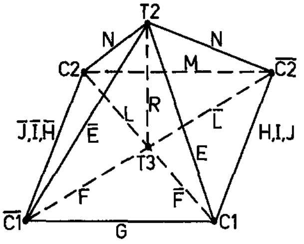

Fig. 8 (see Figs. 6 and 7)

For the $\overline{11}2,234$ mono-chelate system, there are six possible isomers and a tridimensional description of the interconversion paths is needed (see Fig. 8):

The three-dimensional projection of a five-dimensional tetrahedron is also a description of the system, **if** two vertices are excluded ($\overline{C_2} \nrightarrow \overline{C_1}$ and $C_1 \nrightarrow C_2$; *vide infra*).

The complex without any chelating group 112,234 gives eight isomeric forms and the topological representation of the possible interconversion paths may be the three-dimensional projection of a seven-dimensional tetrahedron (see Fig. 9), which is however not convenient in practice.

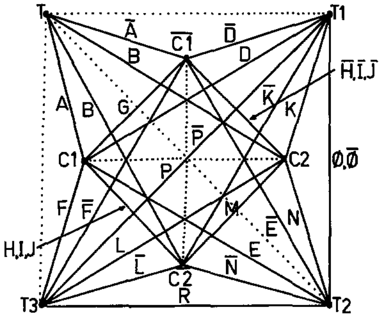

Fig. 9 (see Figs. 6 and 7)

$T_1 = 122,314$ $T = 123,412$

$A = P\,124,231$ $\bar{A} = P\,123,412$

$B = P\,123,241$ $\bar{B} = P\,124,312$

$D = P\,122,413$ $\bar{D} = P\,122,431$

$K = P\,122,314$ $\bar{K} = P\,122,341$

$\phi = P\,132,241$ $\bar{\phi} = P\,123,214$

$P = P\,132,412$ $\bar{P} = P\,123,421$

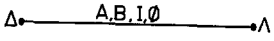

Fig. 10

Another analogous system is the 112,323 one.

With three chelates, there are two possible isomers, $\Delta(\overline{11}\overline{2,\underline{323}})$ and $\Lambda(\overline{11}\overline{2,\underline{33}2})$ and four different transition states or intermediates ($I = P\,123,123$; $A = P\,112,332$; $B = P\,113,223$ and $\phi = P\,122,133$).

A one-dimension graph is thus sufficient to describe the possible isomerizations.

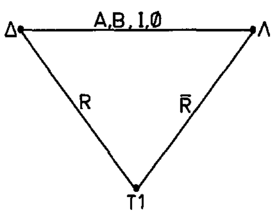

Fig. 11 (see Fig. 10)

With only two chelates [6], three isomers are to be taken into account [5]:

$T_1 = 1\overline{22},\overline{313}$

$R = P\,122,313$

$\bar{R} = P\,122,331$

With one chelating group, there are four different isomers [5] and the situation becomes complicated enough to need a three-dimensional topological representation

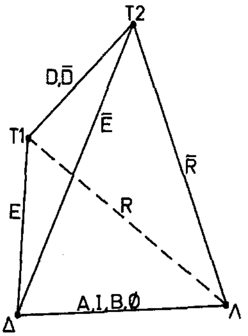

Fig. 12 (see Figs. 10 and 11)

$T_2 = 112,233$

$E = P\,112,233$

$\bar{E} = P\,112,323$

$D = P\,132,231$

$\bar{D} = P\,123,213$

Here again, the number of dimensions which have to be used to describe the complete set of isomerizations of hexacoordinate structures depends on the number of isomers found in a particular system. A one-dimensional description is sufficient for a 112,233 tris-chelate; a two-dimensional graph is necessary for the 112,233 bis-chelate and a three-dimensional tetrahedron is needed for the mono-chelate system. The same system, without any chelate, is described by six different isomers [5] and a five-dimensional tetrahedron must be used (see Fig. 13).

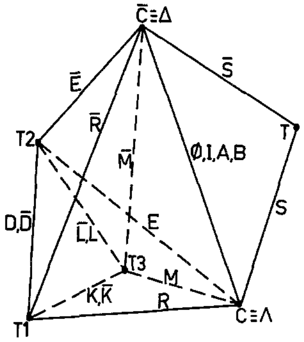

Fig. 13 (see Figs. 10, 11 and 12)

$T = 123,312$

$T_3 = 113,322$

$S = P\,123,231$

$\bar{S} = P\,123,312$

$M = P\,113,322$

$\bar{M} = P\,113,232$

$K = P\,123,321$

$\bar{K} = P\,132,312$

$L = P\,123,132$

$\bar{L} = P\,132,123$

Description of Some Non-Chelate Systems

Some other non-chelate systems have been examined, in order to see whether an increasing complexity is reflected in a higher dimensional graph.

The simplest system is 111,123 (which is analogous to the 111,122 system [5])

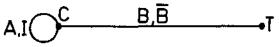

Fig. 14

$C = 111,123$

$T = 112,311$

$A = P\,111,123$

$I = P\,112,113$

$B = P\,112,311$

$\bar{B} = P\,112,131$

The 111;222 system is not more complicated

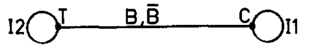

Fig. 15

$C = 111,222$

$T = 112,212$

$I_1 = P\,111,222$

$I_2 = P\,112,221$

$B = P\,112,122$

$\bar{B} = P\,112,212$

A one-dimensional graph is thus sufficient in these cases.

A two-dimensional representation is needed for 111,223, which exists under three isomeric forms [5]

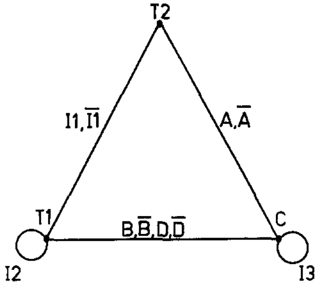

Fig. 16

$C = 111,223$ $T_1 = 113,212$

$T_2 = 112,213$

$A = P\,112,123$ $\bar{A} = P\,112,213$

$B = P\,112,132$ $\bar{B} = P\,112,312$

$D = P\,113,122$ $\bar{D} = P\,113,212$

$I_1 = P\,112,231$ $\bar{I}_1 = P\,112,321$

$I_2 = P\,113,221$ $I_3 = P\,111,223$

A four-dimensional tetrahedron (or a trigonal bipyramid) is necessary to describe the isomerizations of 111,234 (see Fig. 17).

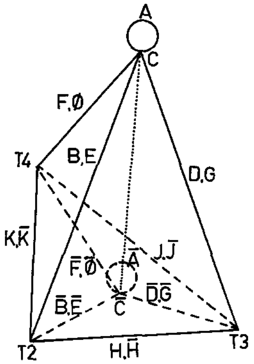

Fig. 17

$C = 111,234$

$\bar{C} = 111,243$

$T_2 = 113,412$

$T_3 = 112,413$

$T_4 = 113,214$

$A = P\,111,234$

$B = P\,113,412$

$\phi = P\,113,124$

$D = P\,114;213$

$E = P\,114,132$

$F = P\,112,314$

$G = P\,112,143$

$H = P\,114,231$

$J = P\,112,341$

$K = P\,113,241$

The general description of the n possible stereoisomers in octahedral species may thus be given by a hypertetrahedron in a $n-1$-dimensional space projected into a three-dimensional one.

For the most general and most complicated six-coordinate system (123,456) [2], there are no less than 30 different isomers (15 pairs of enantiomorphs), which means that a 29-dimensional tetrahedron might be used which has to be projected 26 times in order to be reduced to a three-dimensional space. From each point, one then theoretically might go to 29 other points if all the paths were equivalent [2]. We have said that it is only possible to transform, by RC_3 rotations [2] of triangular faces in the octahedron, one isomer into *eight* other ones and possibly, an eight-dimensional graph might then be sufficient to represent this system topologically.

The general description of the possible isomerizations of 123,456 (O) (see § 2) are given below

$$O \left[\begin{array}{l} \to 1 \longrightarrow 0, 2, \bar{3}, \bar{5}, \bar{7}, 9, 10, 11 \\ \to 2 \longrightarrow 0, 1, \bar{4}, \bar{6}, \bar{8}, \bar{9}, \overline{10}, \overline{11} \\ \to 3 \longrightarrow 0, 4, \bar{1}, \bar{5}, \bar{7}, \overline{10}, 12, 13 \\ \to 4 \longrightarrow 0, 3, \bar{2}, \bar{6}, \bar{8}, 10, \overline{12}, \overline{13} \\ \\ \to 5 \longrightarrow 0, 6, \bar{1}, \bar{3}, \bar{7}, \overline{11}, \overline{13}, 14 \\ \to 6 \longrightarrow 0, 5, \bar{2}, \bar{4}, \bar{8}, 11, 13; \overline{14} \\ \to 7 \longrightarrow 0, 8, \bar{1}, \bar{3}, \bar{5}, \bar{9}, \overline{12}, \overline{14} \\ \to 8 \longrightarrow 0, 7, \bar{2}, \bar{4}, \bar{6}, 9, 12, 14 \end{array} \right| \quad \text{where} \quad \begin{array}{l} 9 \equiv 124{,}653 \\ 10 \equiv 135{,}624 \\ 11 \equiv 125{,}436 \\ \\ 12 \equiv 125{,}346 \\ 13 \equiv 123{,}654 \\ 14 \equiv 123{,}465 \end{array}$$

Furthermore, one has

$$\begin{array}{rl} 9 \longrightarrow & 1, \bar{2}, \bar{7}, 8, \overline{10}, \overline{11}, \overline{12}, \overline{14} \\ 10 \longrightarrow & 1, \bar{2}, \bar{3}, 4, \bar{9}, \overline{11}, 12, 13 \\ 11 \longrightarrow & 1, \bar{2}, \bar{5}, 6, \bar{9}, \overline{10}, \overline{13}, 14 \\ 12 \longrightarrow & 3, \bar{4}, \bar{7}, 8, \bar{9}, 10, \overline{13}, \overline{14} \\ 13 \longrightarrow & 3, \bar{4}, \bar{5}, 6, 10, \overline{11}, \overline{12}, 14 \\ 14 \longrightarrow & 5, \bar{6}, \bar{7}, 8, \bar{9}, 11, \overline{12}, 13 \end{array}$$

Actually, a five-dimensional tetrahedron may be used to describe these isomerizations, if one places two enantiomorphs on one edge (see Fig. 18a) and if all the permitted one-step transformations starting from one isomer are represented by the rotations of each of the 4 triangular faces which contain the edge bearing that isomer (see Fig. 18b) (one face necessarily contains *six* different

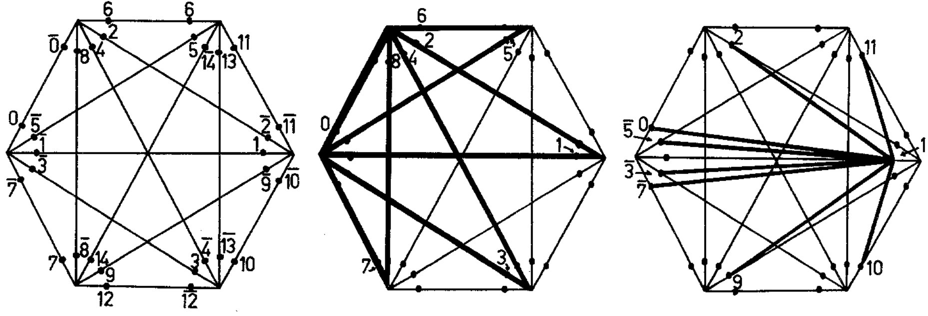

Fig. 18

points for this general systems). This representation is *not* a topological one for the reason that the chemical transformations are described by permutations of the different isomers through a rotation of the faces. In order to get a topological description, one should draw lines connecting the isomers obtained from every one (see Fig. 18c, only eight of the 120 lines have been shown), but this would render the graph rather useless so that we prefer the first representation.

Some of the systems which are described here are being studied experimentally.

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